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Use of Infrared Dyes for Transmission Laser Welding of Plastics

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Abstract

A technique has been developed for transmission laser welding plastics with infrared dye, creating a joint almost invisible to the human eye. Typically carbon black would be used as the absorbing medium for the laser, however, this new approach enables two similar clear (or coloured) plastics to be joined with a minimal mark weld line. A number of dyes have been selected and assessed in terms of strength of light absorption at 1064nm wavelength with an Nd:YAG laser, as well as their visible light absorption. Lap welds have been made in clear PMMA using the infrared dye mixed into methyl methacrylate film as an absorbing medium at the interface between the plastic sheets. The selection of the dyes and processing methods is discussed together with potential application areas.

Historical Review

There are more than fifteen separately identifiable techniques for welding thermoplastics, some of which have been commercially available for many years. These include manual processes such as hot gas welding and extrusion welding, processes using vibration and frictional heating between the materials such as ultrasonic and linear vibration welding and processes using an electromagnetic heat source such as resistive implant welding, dielectric welding and laser welding[1].

Since early in the development of lasers for materials processing (the first multi-kilowatt CO_2 laser was developed at TWI in 1970), it has been shown that lasers may be used for welding plastics[2]. The CO_2 laser (10.6μm wavelength) tends to heat most plastics from the surface down with a very rapid heating action achievable. Thin polyolefin films (up to 0.1mm thick) have been welded with a CO_2 laser at up to 500m/min [3].

Nd:YAG and diode lasers (800-1100nm wavelength) will transmit through several millimetres of unpigmented polymer. The polymer can be designed to absorb and heat in these laser beams with the addition of an absorber. Transmission laser welding of thin and thick materials is therefore possible where a transmitting plastic overlays an absorbing plastic. This results in a method of welding plastics that does not use mechanical vibration and does not mark the outer surfaces of the component. The melting is carried out only where is required on pre-assembled parts. This process was first described in 1985 for welding automotive components [4].

Typically carbon black pigment is used as the additive to enhance absorption for transmission laser welding [5]. An example is shown in Figure 1. The requirement for two different coloured materials at the joint is a limitation for the process in applications where appearance is important. Dyes have been used that appear black but transmit infrared[6], which allows all-black components to be welded. The first (published) part mass produced using transmission laser welding was a keyless entry case for Mercedes in 1997[6]. This paper

describes the selection and use of organic dyes for laser welding that appear clear but absorb infrared, which allows completely clear or similar coloured components to be welded.

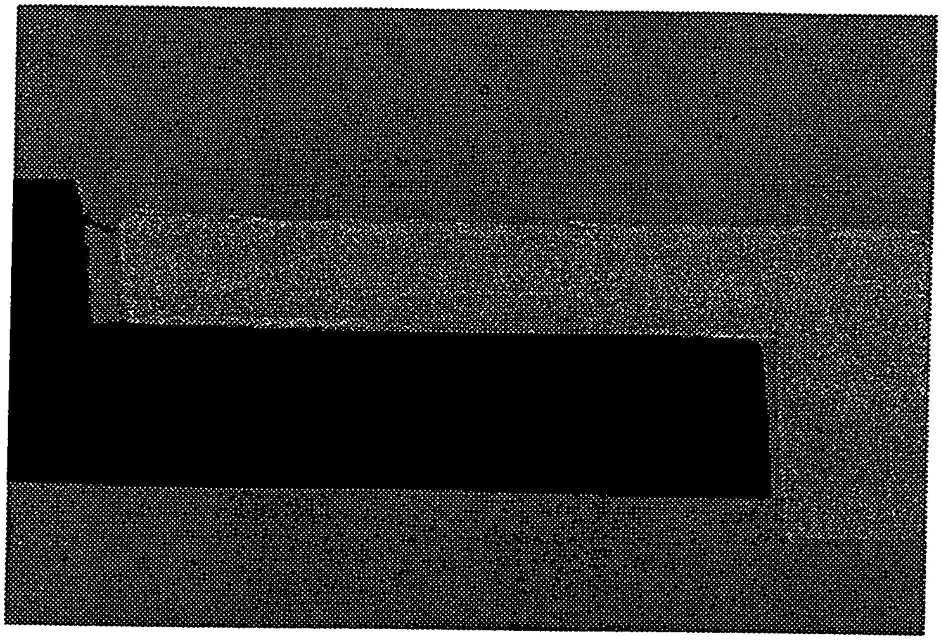

Fig.1 Laser transmission weld in 4mm thick polypropylene using a 100W Nd:YAG laser at 1.6m/min. The weld is at the interface between the light and dark materials.

Light Absorption and Energy Conversion in Organic Dyes

Conventional dyes, by definition, absorb visible electromagnetic radiation (380 – 750nm), the process involving excitation of a π-electron from the highest occupied molecular orbital of the chromophore into the first vacant antibonding π^* orbital. The process occurs without electron spin change and the dye is promoted from the singlet ground state (S_o) to the first excited singlet state (S_1). The energy increase is quite considerable (*ca.* 150-300kJ.mol^{-1}), and the dye molecule must lose the energy rapidly by various processes, returning to the ground state, when it is available to absorb a photon of light again. The most common deactivation process is *internal conversion*, followed by *vibrational relaxation*, in which the molecule passes from the zero vibrational level of the S_1 state into a high vibrational level of the S_o state, and then undergoes rapid vibrational relaxation (*ca.* 10^{-13} seconds) to the lowest vibrational level of S_o, with the excess thermal energy being transferred to the surrounding host molecules. (Other deactivating processes, such as fluorescence, or vibrational relaxation via the triplet state (*intersystem crossing)* are generally less important for most dyes.) The overall effect is for the host matrix to become heated, and the local temperature rise will be determined by the wavelength and intensity of the light, and the thermal conductivity of the host. This phenomenon has been used extensively in *heat mode optical data recording*, where a finely focussed laser beam is absorbed by a dye and the heating effect produces a change in the polymer substrate, by melting or ablation. It has been shown, for example, that writing energies as low as 0.1 nanojoule per square micron can produce local temperatures up to ca, 300°C, sufficient to melt most plastics and dyes, if a dye layer absorbing some 99% of the incident energy is employed[7].

For maximum conversion of light energy to thermal energy by a dye, the dye should absorb as much of the light as possible, and if broad band radiation is employed then the naturally broad bands of most dyes is an advantage. However, if laser sources are employed then it is important to match the λ_{max} of the dye as closely as possible to the laser wavelength. In addition, a narrow band dye is likely to have a much higher molar absorption coefficient at its λ_{max} than a structurally similar dye with a broad absorption band, and consequently less dye will be needed to achieve maximum absorption of the incident light.

Infrared dyes have played a major role in he development of optical recording systems, as the first economical lasers were infrared emitting. The introduction of low cost diode lasers emitting near 800nm resulted in an explosion of research interest in new dyes absorbing in this region. Today, as red, green and even blue, diode lasers are becoming more commonplace, the need for infrared dyes as electronic/thermal energy converters is becoming less, but is unlikely to disappear altogether. This is because infrared dyes have the valuable advantage (in many cases) of minimal visual colour, and for some applications an absence of colour is an essential requirement.

Although infrared absorbing pigments are known, and do offer distinct stability advantages over infrared dyes, their drawbacks are considerable. A classical example is carbon black, which absorbs visible and near infrared light. The particulate nature of such pigments means that light scattering occurs and light absorption efficiency is reduced. In addition the low molar absorption coefficients of pigments means that higher concentrations have to be used to produce a given heating effect, and apart from the cost disadvantages, this can lead to undesirable changes in the physical properties of the host, including the appearance of unwanted colour. The residual colour problem is particularly true in the case of carbon black.

Selection of Near-Infrared Dyes for Laser Welding

The ideal near-infrared dye for laser welding of transparent plastics would have the following attributes:

- A narrow, absorption band near 800nm, (or longer wavelengths, depending on the laser used) with a high molar absorption coefficient.
- Little if any absorption in the region 400-700nm.
- Good solubility in the host.
- Good stability towards the incorporation method used.
- Should not degrade to coloured by-products.

If all the known near infrared dye systems are considered, the vast majority can be discounted on the grounds that they have pronounced visual colour. Others can be disregarded because of their instability or their low absorption intensity. Selection of the most appropriate candidates from the remainder then becomes a matter of trial and error. Examples of three dye types which can satisfy all of the above requirements are the cyanine dyes, e.g. (Fig.2), the squarylium dyes (Fig.3), and the croconium dyes (Fig.4).

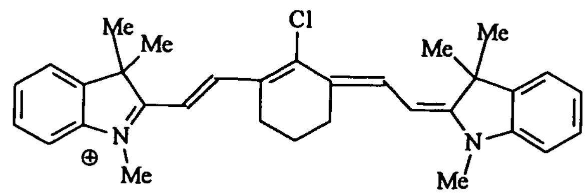

Fig.2 Example of cyanine dye [λ_{max} = 785nm; ε_{max} = 360,000 $l.mol^{-1}.cm^{-1}$ in dichloromethane]

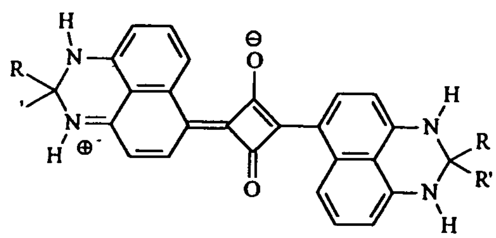

Fig.3 Example of squarylium dye [λ_{max} ca. 800nm; ε_{max} = ca. 150,000 $l.mol^{-1}.cm^{-1}$]

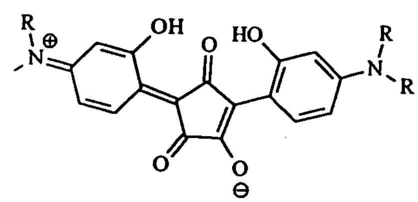

Fig.4 Example of croconium dye [λ_{max} ca. 820nm; ε_{max} = ca. 200,000 $l.mol^{-1}.cm^{-1}$]

Methods of Introducing Dyes for Plastics Welding

Near infrared absorber dyes have the properties of absorbing light in the region beyond 780nm with high efficiency. That is, they have high extinction coefficients at one or many wavelengths in that spectral region. When this light is absorbed whether it be from a laser source or an incoherent light source, the molecules dissipate the absorbed energy principally as heat via vibronic relaxations, and this heat is localised to the dye molecules and to their immediate host environment. In the case where the host is a polymer (most thermoplastics and some highly crosslinked polymers as well), a melting occurs at the surface where the dye and polymer are. If a clear polymer (i.e., one that does not absorb NIR radiation but which may simultaneously be water white or coloured) is adjacent to this surface, the melting will cause a weld to occur.

Thus, in order to have the weld occur, the dye must be absent from the front plastic entity allowing the laser light to pass through it unabsorbed and must be localised at least at the surface of the other plastic entity or at the interface between the two plastic pieces. In this sense, the lamina of dye is essentially behaving as an optical focal element for the laser

light, absorbing it very efficiently in an extremely thin layer and converting the absorbed light to heat in that same layer. The laser light as well as other wavelengths of light are otherwise effectively transmitted by the remainder of the ensemble which lies in front of this laminar surface as well as behind this surface (an exception to the latter is when the option is used in which one element to be welded has its bulk pervaded by the dye). The establishment of such a dye-laden laminar surface can be accomplished in several ways:

- The dye can be incorporated into a thin film which can be placed at the interface of the plastic pieces to be welded. The film substrate can be the same polymer(s) being welded but may also be a different polymer. Dye concentrations of approximately 0.02% on a film weight basis are typically adequate but are a function of the particular dye used as well as the plastics being welded. A film thickness of approximately 25μm is also typical. The advantage of using a film/tape containing the absorber dye is that the dye is needed in the film only where there is to be welding and its carrier is a solid allowing for ease of handling, storage, etc. Another advantage is that both plastic pieces can be of the same material and may notably be transparent plastic. A disadvantage is that film or tape whether it be free standing or a transfer film containing the dye can be difficult to apply especially to other than non-ruled surfaces.

- The dye can be introduced into the bulk of the polymer of the latter of the two polymer pieces (latter in terms of which one the laser light encounters). Only that dye at or very near the surface is active at absorbing the laser light since the dyes are highly efficient NIR absorbers. The light absorption results in the weld as before but without the use of tape/film. The advantage is that there is no extra step in the welding manufacturing having to do with application of tape, etc. A disadvantage is that much more dye is used in that it pervades the entirety of the second substrate piece and therefore is costlier. Another is that there this substrate piece will have a denser colour than if the dye were not in it.

- The surface of the latter plastic piece can be made, for instance, by having a dye laden film used as a mould insert in a moulding operation to generate the dye rich surface on the plastic piece. While admitting no extra step in welding, this makes for a more costly moulding operation.

- The surface of one of the substrates to be moulded may be imparted a surface application of the dye by dip coating, dye infusion, painting, spraying, printing, dry burnishing, paste application, etc. This is a low cost alternative in terms of dye used and offers flexibility in that only selected areas can be treated. However, extra processing steps are required before the welding step and stability of a treated but not yet welded piece in storage would have to be evaluated on a case by case basis.

- The material to be welded can be coextruded with polymer containing the dye, but this can restrict the approach to certain applications able to make use of the extruded form.

- A plastic piece can be overmoulded to provide a narrow strip, for example, to a selected area, but this encounters a higher moulding cost.

Clearly, the method which is employed would depend on the particular application and the restrictions of cost, colour, extra manufacturing steps, etc.

Description of the Laser Welding Process

In the pre-weld construct the dye layer at the interface between the materials acts as the site where the light from the laser is very efficiently absorbed and converted into heat in a well defined and confined area. The area of heating may be defined by either the size of the laser beam or the extent of the dye-containing region. Welding occurs as a result of the heat generated giving melting of the plastic material up to a depth of typically 0.2mm. Where compatible material is in good contact interdiffusion of molecules and hence welding will occur (Fig.5). The heat generation at the weld interface is controlled by the absorption coefficient of the dye layer, and the processing parameters. The main parameters are laser power, which is typically between 10W and 500W, the welding speed (typically 5-200mm/sec) and the spot size of the laser beam (0.5-10mm wide). Processing can also be carried out with a fixed laser array, which would irradiate the joint area for a defined time.

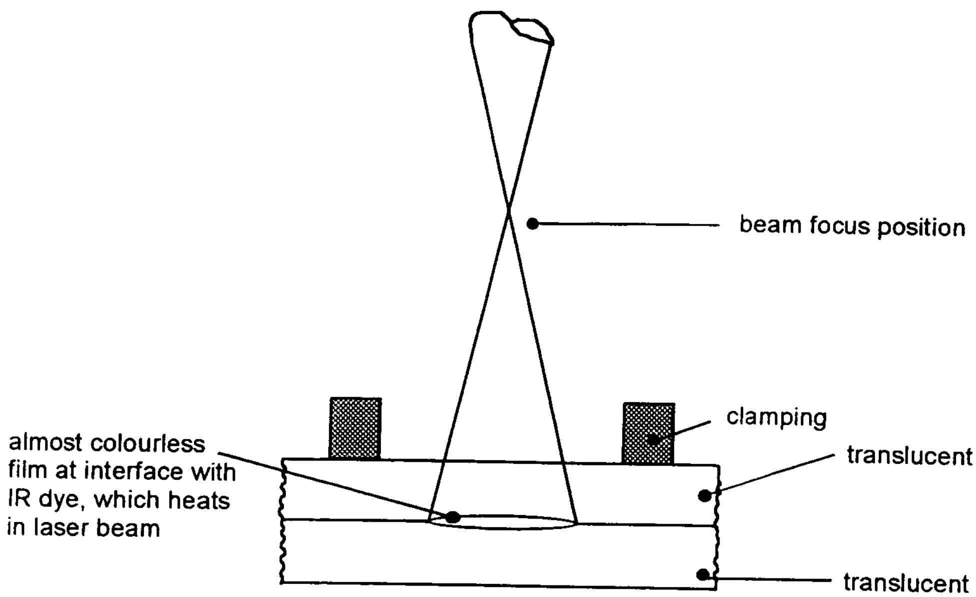

Fig.5 Diagram of transmission laser welding process using infrared dye.

Results of Welding Trials

Plates of polymethylmethacrylate (PMMA) of 3mm thickness were welded using a Nd:YAG laser using its fundamental 1064nm wavelength. A thin film of methylmethacrylate (MMA) containing the NIR absorber dye was placed at the interface of the pieces to be welded. The dye concentration and film thickness were as described above. The film strip width was 5mm and the laser beam was round with a diameter of approximately 6mm. It was positioned to be absorbed, heat and melt the full width of the film (Fig.6). The temperature profile at the weld interface has been estimated using a finite element model of the welding process (Fig.7).

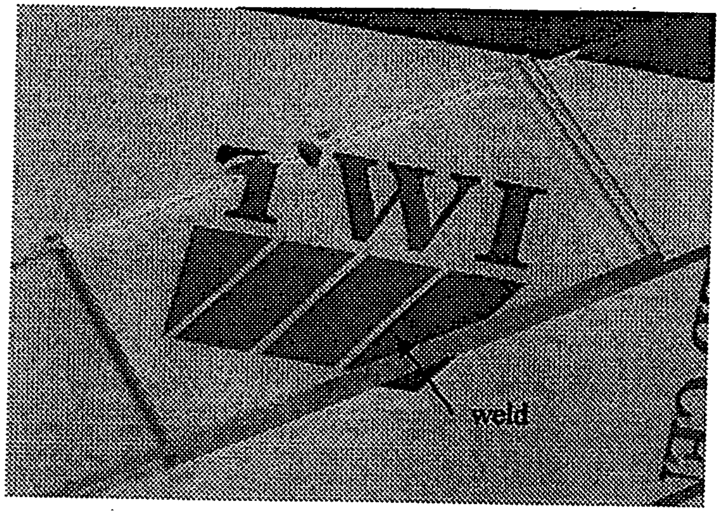

Fig.6 Transmission laser weld in PMMA made with infrared dye impregnated film at the interface.

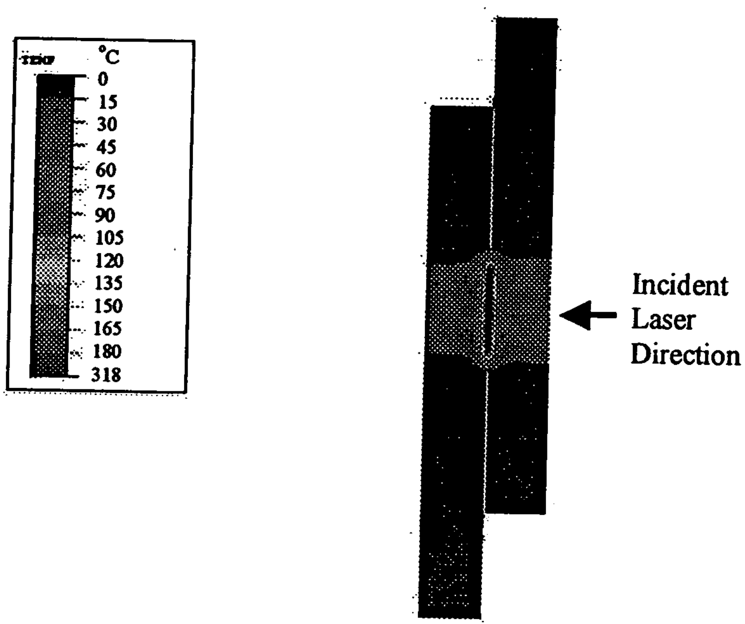

Fig.7 Estimate of the thermal profile of laser weld using infrared dye from finite element analysis.

The visible and NIR spectra of the substrate/film/substrate ensemble were measured before and after the welding and may be observed in the appended typical spectra. The low concentration of the dye in the film make ready discrimination of the differences in these spectra difficult. However, spectral measurements of the colour coordinates through the welded parts show a neutral colour result of the weld. Analyses on the molecular fate of the dyes having undergone the welding procedure are underway, however we believe that the dyes at this interface will have been decomposed to colourless organic molecules from the temperatures believed to have been attained at the weld interface.

Welded samples have been tensile tested using standard procedures. Failure is observed to occur not across the weld interface but in the parent material near the edge of the weld (Fig.8). The failure force was 50N per mm weld width.

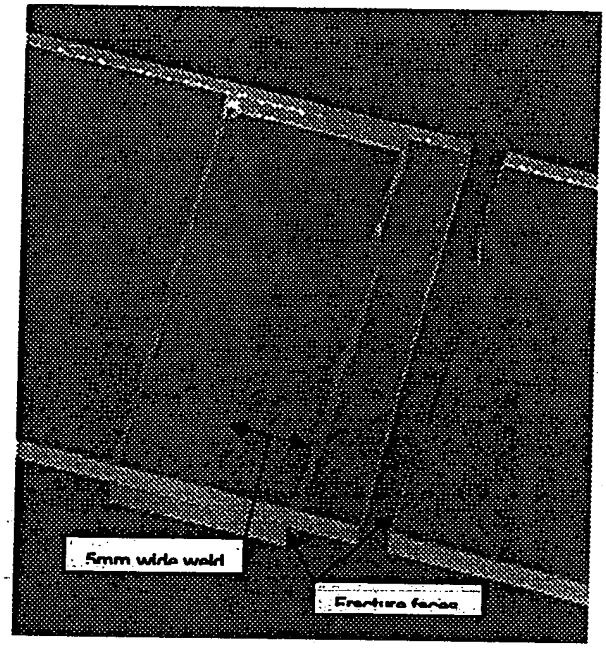

Fig.8 In tensile testing of a lap weld in PMMA made with infrared dye impregnated film at the interface, the failure position is in the parent material at the edge of the weld.

While the above examples are focused on PMMA plaque welding examples using FILTRON™ NIR absorbing film at the interface, the welding technique (termed ClearWeld™) has also been used for welding nylon based fabrics (laser stitching/sewing/seam-sealing/etc.) and thin films (PE, PEEK). In these cases the dye was dissolved in a suitable solvent and painted over the joint region with resultant deposition of dye both at the surface and infusion of dye very slightly into the substrate. It was allowed to dry prior to welding. Clearly, use of polymeric substrates such as polyester, polycarbonate, polystyrene, polysilicones, etc. either alone or in textile or other blends and numerous thermoplastic films are obvious extensions of this example. It should be noted that while maximum dye utility is attained when the dye is truly dissolved in the substrate (film or bulk or other carrier), suspensions of dye applied in these modes are also efficient for the welding applications described above.

Summary

Plastics may now be laser welded using the ClearWeld™ technology with NIR absorbing dye positioned at the interface in a suitable manner. The weld produced can be clear and has very little affect on the appearance of the product being welded. There is a wide range of methods for the insertion of the dye at the joint interface, which allows for flexibility in use over a range of potential applications. The welding process relies on available technology and the dye may be used without compromising the strength of the joint.

A patent has been applied for by TWI for the process. To date the techniques for using the dye with laser welding are being developed in collaboration between TWI (welding development) and Gentex (dye development).

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